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(19) (CA) **CANADIAN PATENT** (12)

(54) Liquid Thickeners Based on Diurethanes and Process of
Praparing the Same

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ABSTRACT

Liquid thickeners based on diurethanes are prepared by alkoxylation of monovalent alcohols with 8 to 30 carbon atoms with a mixture of ethylene oxide and propylene oxide, wherein the molar ratio of ethylene oxide to propylene oxide in the mixture is approximately 30 : 70 to 90 : 10 and 20 to 200 mol alkylene oxides are used per mol alcohol, and the resultant polyether is reacted in a molar ratio of 1 : 0.7 to 1 : 0.25 with a diisocyanate. Hexamethylene diisocyanate is particularly suitable as the diisocyanate. The thickeners can be used especially for the thickening of aqueous systems. Thickeners with widely differing properties can be prepared by blending two or more such diurethanes.

LIQUID THICKENERS BASED ON DIURETHANES AND PROCESS OF PREPARING THE SAME

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to thickeners, especially liquid thickeners, which have been obtained by alkoxylation of alcohols with a mixture of ethylene oxide and propylene oxide, as well as further reaction of the resultant polyether with diisocyanates and their use as thickeners in aqueous systems.

2. Description of the Prior Art

In European Laid-Open Application EP-OS 31,777 of July 8, 1981, polyoxyalkylene glycol block polymers are described which, by reaction of polyglycols with a stoichiometric deficit of polyisocyanates, especially aromatic diisocyanates, are transformed to corresponding high molecular weight polyurethanes with terminal OH groups. These polyurethanes can be used as thickeners, especially for aqueous systems.

An important disadvantage of these water-soluble polyurethane thickeners is their poor thickening effectiveness so that, in order to be able to adjust specified viscosities, relatively large quantities of these polyurethanes must be used, leading to an increase in cost of the thickening process.

Furthermore, the polyurethanes described in European Laid-Open Application EP-OS 31,777 are highly viscous substances, which are not pumpable and are thus difficult to process and to meter.

Another disadvantage of these high-molecular-weight polyurethanes is that they have a relatively low shear stability. Thickeners with a high shear stability are particularly needed in many technical applications, e.g., in hydraulic fluids. Also, problems are associated with the synthesis of these polyurethanes since their properties depend to a large extent on the degree of polymerization and on a large number of other factors. For example, when preparing these polyurethanes, the diisocyanate reactivity, the OH number, the purity of the feed products, the catalyst used and other process parameters, such as temperature and



the like, play a major role, so that reproducibility, when synthesizing polyurethanes, can only be assured with difficulty.

West German Laid-Open Application 1,444,243 of October 24, 1968, describes reaction products of aromatic, hydroaromatic or aliphatic mono- or polyisocyanates with high-molecular-weight alkoxylation products of compounds which contain at least 8 carbon atoms and which have only one hydrogen atom capable of reacting with alkylene oxides. Compounds such as ethyl isocyanate, stearyl isocyanate, toluylene diisocyanate, hexamethylene diisocyanate or 4,4'-triisocyanatotriphenylmethane, among others, are cited as isocyanates. The alkoxylation products are addition products based on monohydric alcohols, carboxylic acids, phenols, mercaptans or secondary monoamines, to which either ethylene oxide or propylene oxide has been added. The products described therein are used as adjuvants in the dyeing or printing of textile materials. Essentially similar products are recommended in West German Laid-Open Application DE-OS 2,054,885 of May 10, 1972 as agents for pigment printing pastes.

However, the syntheses described in West German Laid-Open Application DE-OS 1,444,243 or 2,054,885 lead to pasty or solid products with the disadvantages associated therewith, e.g., for use as thickeners. They are not pumpable and therefore they cannot, as a rule, be mixed directly with additives such as solubilizers and co-thickeners. Their intermixability in aqueous systems leaves something to be desired.

Also, when preparing such urethanes, the use of a catalyst is usually necessary, so that thickeners are obtained which in some form still contain the undesired catalyst, which frequently cannot be removed at all or only with the greatest difficulties.

Although a large number of thickeners are already known, there is still a need for thickeners with improved properties, as well as for advantageous fabrication processes, especially for thickeners which are fluid and can be processed in aqueous systems without problems.

SUMMARY OF THE INVENTION

It is therefore an object of this invention to provide thickeners or thickener mixtures which are particularly suitable for the thickening of aqueous systems, are universally usable, can be intermixed rapidly and completely at room temperature or at a slightly higher temperature, and with which reproducible adjustments of desired viscosities in solutions and dispersions are possible.

Another object of the invention is to provide thickeners which are relatively insensitive to temperature or concentration fluctuations, i.e., which possess a viscosity which fluctuates only slightly during changes in temperature or concentration.

Another object of the invention is to provide thickeners which possess a high degree of effectiveness, which are stable under shear, and can be handled simply, i.e., which are extremely fluid and have a particularly low viscosity, so that they can be easily pumped and metered.

Another object of the invention is to provide a process by which such thickeners can be synthesized simply, economically and reproducibly.

Another object of the invention is to provide thickeners which, particularly when mixed with one another, will lead to mixtures with controllable properties.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 graphically displays the viscosity of various citric acid solutions as a function of thickener concentration and temperature; and

Figure 2 graphically displays the viscosity of 14% ether sulfate solutions as a function of thickener concentration and temperature.

DESCRIPTION OF PREFERRED EMBODIMENTS

The above and other objects are achieved by a process for synthesizing thickeners, especially liquid thickeners, by the alkoxylation of alcohols with alkylene oxides, and by the reaction of the resultant polyether with diisocyanates. Specifically, monohydric alcohols having 8 to 30 carbon atoms are alkoxyated with a mixture of ethylene oxide and propylene oxide, wherein the molar ratio of ethylene oxide to propylene oxide in the mixture ranges from approximately 30 : 70 to 90 : 10, and 20 to 200 mol of alkylene oxide are used per mol of alcohol, and the resultant polyether is reacted with a diisocyanate in a molar ratio of 1 : 0.7 to 1 : 0.25.

Preferably, alcohols with 10 to 20, and especially with 12 to 18, carbon atoms are employed. It is advantageous to use 60 to 120 mol of alkylene oxide per mol of alcohol. Advantageously, a molar ratio of ethylene oxide to propylene oxide of 50:50 to 90:10, and preferably of 70:30 to 85:15, yet especially of 80:20 to 85:15, is used.

Hexamethylene diisocyanate is particularly suitable as the diisocyanate.

Advantageously, tallow alcohol and lauryl alcohol are used as alcohols within the scope of the invention. Mixtures of alcohols, especially mixtures of lauryl and tallow alcohol, are preferred.

The subject matter of the invention also comprises liquid thickeners which can be obtained by a process according to one of claims 1 to 12.

The liquid thickeners of the invention are particularly suitable for the thickening of aqueous systems, wherein a preferably surface-active solubilizer is advantageously employed. Alcohol alkoxyates, especially alcohol ethoxyates, are particularly suitable as the solubilizer.

In an advantageous embodiment of the invention, mixtures of the thickeners are used.

The synthesis of the alkoxyated alcohols needed as intermediate product is carried out according to processes which are known in the art. For example, an alcohol such as tallow alcohol, is alkoxyated with a mixture of ethylene oxide and propylene oxide; in the process, relatively high temperatures, e.g., of 140° to 180°C are generally applied, and a suitable catalyst, preferably of basic nature, e.g., KOH or CH_3ONa , is used. It is advisable to carry out the alkoxylation under pressure, e.g., at 3 to 5 bar.

The molecular weight of the alkoxyated alcohol can be varied within relatively wide limits. Advantageously, the molecular weight is adjusted to approximately 2,500 to 5,000.

In addition to the preferred alcohols (i.e., tallow alcohol and lauryl alcohol being the two alcohols which are preferably used in a mixture), one may use other alcohols within the scope of the invention, namely native alcohols and synthetic alcohols. For example, the C_8 to C_{30} alcohol cuts, and more preferably the C_{10} to C_{20} alcohol cuts obtained in technical syntheses, oxoalcohols and guerbet alcohols may also be used. Other alcohols that may be employed are, for example, myristyl, stearyl alcohol, etc.

In addition to the two catalysts mentioned earlier, basic compounds such as KOH, or alcoholates such as KOCH_3 , or even Lewis acids such as BF_3 , may also be used.

The proportion of catalyst used is generally around 0.2 to 0.5 weight percent relative to the alcohol used.

The resultant polyether is then neutralized by processes known from the prior art, using approximately 50 to 200 ppm of benzoyl chloride relative to the polyether (see W. Foerst, Ullmanns Encyclopaedie der techn. Chemie Vol. 14, page 341, Verlag Urban, Schwarzenberg, Munich, 1963). Then, after the catalyst has been removed, a reaction is carried out with a diisocyanate. The reaction temperature is generally 60° to 100°C, and preferably the reaction is carried out at approximately 80°C.

The ratio of OH compound to diisocyanate is generally 1 : 0.7 to 1 : 0.25, and preferably the ratio of OH compound to diisocyanate is approximately 1 : 0.55, i.e., 10% more than one-half mol of diisocyanate is used per mol of polyether.

In addition to the aforesaid hexamethylene diisocyanate, which is preferred and which leads to odorless and colorless products, other aliphatic, cycloaliphatic and aromatic diisocyanates can also be used, toluylene diisocyanate and diphenylmethane diisocyanate being particularly suitable.

Advantageously, the urethanes obtained in this way are used as thickeners in aqueous systems. Such aqueous systems include aqueous surfactants, aqueous alcoholic systems, especially mixtures of ethylene glycol and water, acids such as phosphoric acid, citric acid, aqueous electrolyte solutions, polyacrylate dispersions, and the like.

In many cases, it is advisable to additionally use a solubilizer, which is most effectively employed in the form of a thickener premix. A thickener premix is a mixture of the actual thickener and the solubilizer which, before it is added to the solution or dispersion to be thickened, is prepared separately. These premixes can be prepared for storage, and have a particularly long shelf life.

The intermixability of the thickener in the formulation is simplified by the use of thickener premixes, i.e., the thickener premix can be intermixed rapidly, particularly at room temperature. The intermixability of highly effective diurethane thickeners, which generally require relatively high temperatures and relatively long stirring times, is simplified by this process and thus they are rendered more cost-effective.

In many cases, it is of advantage to utilize a solubilizer of a nonionic nature, especially if the solubilizer and the thickener are to be intermixed separately in the formulation.

If premixes are prepared first, anionic solubilizers are very suitable in addition to the preferable non-ionic solubilizers.

The use of solubilizers is particularly recommended if aqueous systems which do not contain a surfactant are to be thickened.

Particularly advantageous within the scope of the invention, are thickeners comprised of mixtures of at least two diurethanes.

In this way, one can prepare thickener systems with a completely defined property profile, with which the most diverse requirements of technology can be met.

The preparation of such mixtures is possible, first of all, by using two different alcohols, especially lauryl and tallow alcohol, as starting materials as early as the synthesis stage, and alkoxyating these two alcohols either separately or together with a mixture of ethylene oxide and propylene oxide; this mixture is then made to react with the diisocyanate.

Preferably, however, the mixtures are made by preparing a mixture of two or more diurethanes according to the present invention. In this way, a high degree of flexibility is achieved, and practically any desired number of thickener systems can be obtained simply by mixing in different concentration ratios.

Thus, it is possible to obtain, in a simple fashion, thickener systems which are easy to handle; and which, for example, can be adjusted to a low viscosity and made pumpable, and which, depending on the mixture's composition, have the desired properties for technical application, e.g., they are intermixable at room temperature, have a high degree of thickening effectiveness, have a reproducibility of the desired viscosity, which ensure stability of the viscosity of the formulations within a given temperature range, which are insensitive to fluctuations in concentration, etc.

The thickeners according to the invention can easily be processed with other common additives, both as a premix and also alone or in mixtures.

The diurethanes according to the invention are stable within wide pH ranges. They are colorless, clear compounds which are liquid at room temperature and, when intermixed in aqueous systems of pH 1 to 10, are stable to hydrolysis.

The invention will be discussed in greater detail with reference to the examples below, which are presented only for illustration, and not for limitation.

EXAMPLE 1A AND 1B

Synthesis of the thickeners according to the invention

The quantities used in Examples 1A and 1B are listed in Table 1 together with other specifications. First, the alcohol in the liquid state is mixed in an autoclave with 0.3 weight percent of KOH and dehydrated for 60 min at 70 to 120°C and 10 to 20 torr. Then, the vacuum is eliminated by the introduction of nitrogen and the appropriate quantity of a mixture of ethylene oxide and propylene oxide is added in metered portions at 150°C and 3 to 5 bar.

At the end of the addition and after reaction, the product is cooled.

Thereafter, the liquid alcohol alkoxylate is transferred to a three-necked flask provided with a stirrer and a reflux condenser and the apparatus is evacuated briefly to approximately 10 to 20 torr.

Subsequently, the vacuum is eliminated by the introduction of nitrogen, and 100 ppm of benzoyl chloride is added, while stirring. Thereupon, the diisocyanate is metered in at 80°C for 10 minutes. After a 2-hr post-reaction at 100°C, the product is cooled to 40°C, decanted and analyzed.

Table 1: Experimental and product data for two selected diurethane thickeners
 $R_1(EO, PO)_{a/b} Y(EO, PO)_{c/d} R_2$

Reaction product	A	B
Alcohols – R_1, R_2	Tallow	Lauryl
(g)	261	197
Catalyst (g, KOH)	0.8	0.8
EO, PO (ratio a/b, c/d)	66/14	66/14
(g)	3721	3721
Alkoxyate:		
Molecular weight	3980	3920
Viscosity (cSt/20°C)	1140	1090
Pour point (°C)	9	9
Cloud point (°C)	79	80
(1% in water)		
Diisocyanate Y	HMDI	HMDI
(g)	96.7	96.7
Alcohol/diisocyanate	1 : 0.55	1 : 0.55
Benzoyl chloride (ml)	0.4	0.4
Diurethane:		
Molecular weight	8130	8010
Viscosity (cSt/20°C)	7800	7600
(cSt/40°C)	2750	2750
Pour point (°C)	10	10
Tallow alcohol:	Alcohol mixture $C_{16}-C_{18}$	
Lauryl alcohol:	Alcohol mixture $C_{12}-C_{14}$	
HMDI:	Hexamethylene diisocyanate	

EXAMPLE 2

A clear, viscous and pumpable solution is prepared with brief stirring comprising 90 parts of the liquid thickener A and the liquid thickener B, as well as 10 parts of water. The solution can be stored indefinitely and shows no tendencies toward separation.

The solutions can be blended with solubilizers or co-thickeners to form premixes.

The premixes can also be stored indefinitely and, when needed, can be used directly without further treatment.

EXAMPLE 3

Various thickened aqueous systems are prepared from the diurethanes A and B according to Example IA and IB simply by intermingling the diurethanes.

The viscosity of the solutions was determined in the Ubbelohde viscosimeter at temperatures of 20°C and 38°C. The results and other data are listed in Table 2.

The systems in Example IV of Table 2 are dispersions; in this case, the viscosity was determined with the Brookfield viscosimeter. The viscosities are indicated therein in mPa.s.

Table 2: Thickening of aqueous systems with the thickeners A and B

Example	Solution to be thickened	Concentration of solution	Thickener/ solubilizer	Concentration of the thickener/ solubilizer	Viscosity in cSt 20°C	38°C
I-1-a	Hydrochloric acid	10%	A/C	2% / 2%	233	-
1-b			A/D	2% / 2%	1666	-
2-a	Phosphoric acid	10%	A/E	2% / 2%	1920	-
3-a	Citric acid	5%	A/F	2% / 1%	517	-
			A/F	3% / 1%	10487	-
			B/F	5% / 1%	587	-
			B/F	5% / 2%	652	-
II-a	Ethylene glycol	47%	A/C	3% / 3%	292	-
-b			B/-	6% / -	429	142
-c			B/E	4% / 2%	-	76
III-1-a	Lial Alcohol ^{*5}	5%	A/-	2% / -	4701	-
1-b	ethoxylate	10%	A/-	2% / -	2627	-
1-c	(- 7 EO -)		B/-	5% / -	1703	-
1-d		14%	A/-	2% / -	2572	-
1-e			B/-	5% / -	1315	-
2-a	Lial alcohol ^{*5}	5%	A/-	3% / -	17513	-
2-b	ethoxylate	14%	A/-	3% / -	2652	-
	(- 12 EO -)					
3-a	Ether sulfate ^{*1}	5%	A/-	3% / -	2630	-
3-b		14%	A/-	3% / -	275	-
3-c			B/-	5% / -	1375	-
4-a	Quaternary ammonium salt ^{*2}	25%	A/-	2% / -	601	-
5-a	Quaternary ammonium salt ^{*3}	0.5%	A/-	3% / -	1690	-
5-b		2.5	A/-	2% / -	393	-
IV-a	Polyacrylate	-	A/-	0.01%/-	104 ^{*4}	-
-b	dispersion	-	A/-	0.1%/-	13000 ^{*4}	-
-c		-	B/-	0.1%/-	830 ^{*4}	-
-d		-	B/-	0.3%/-	400000 ^{*4}	-

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Supplement to Table 2:

Solubilizer:	C	Tallow alcohol ethoxylate, 60 EO	(Akzo Chemie: ELFAPUR T 600)
	D	Trimethyltallowammonium chloride	(Akzo Chemie: ARQUAD T 50)
	E	Nonylphenol ethoxylate, 12 EO	(Akzo Chemie: ELFAPUR N 120)
	F	Didecyldimethylammonium chloride	(Akzo Chemie: ARQUAD 2-10/50)
Notes:	*1	Sodium C ₁₂ /C ₁₅ fatty alcohol ether (2,5) sulfate	(Akzo Chemie: ELFAN NS 252)
	*2	Didecyldimethylammonium chloride	(Akzo Chemie: ARQUAD 2-10/50)
	*3	Dimethylaurylbenzylammonium chloride	(Akzo Chemie: ARQUAD DMMCB-50)
	*4	Brookfield viscosimeter	dynamic viscosity in mPa.s
	*5	Lial alcohol = keto alcohol with C ₁₂ to C ₁₃	

* The terms Elfapur, Arquad and Elfan are all trade-marks.

EXAMPLE 4

Mixtures of thickeners, processed by the methods described in Example 2, permit control of a requirements profile for the solution to be thickened.

It is shown in Figures 1 and 2 how the two thickeners A and B, the thickening effect of which was listed in Table 2, work together.

The first system, which is described in greater detail herein, consists of a 5% citric acid solution, which is mixed with 1% didecyldimethylammonium chloride and is thickened with a mixture of A and B. If the ratio $A : B = 1 : 2$ with a total activity of 3% is chosen, a viscosity of 260 cSt at 20°C (3-I) is obtained. At 30°C (3-I), the viscosity decreases to 90 cSt (a reduction by 65%).

Using this reference system (3-I) as a basis, the quantity of B is increased by 1%. Example 3-II shows that, on the one hand, the viscosity increases only by ca. 20% but, on the other hand, the tolerance of the overall system to temperature rise is improved (a reduction by 39%).

If the quantity of A is increased by 1% (Example 3-III), the viscosity increases considerably, but the temperature profile remains unchanged.

The influence of thickener B on the viscosity-temperature profile, which is shown in Figure 1, is confirmed in Figure 2. The kinematic viscosity, measured in cSt, as a function of different mixing ratios of A and B is plotted herein. The thickened surfactant is an ether sulfate (14%).

The tolerance to temperature of a mixture of thickener A and thickener B runs parallel with a tolerance to the composition of the mixture: if the proportion of B is high, the viscosity is independent of the mixing ratio over a wide mixing range. Example 3-IV shows that the sensitivity to concentration fluctuations becomes greater with increasing proportion of the relatively more effective thickener A.

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Both Figures show that a combination of two thickeners, in this case A and B, permits adjustment of the viscosity and the tolerance of the thickened system.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A liquid thickener comprising the diurethane reaction product of a polyether and a diisocyanate in a molar ratio of 1 : 0.7 to 1 : 0.25, wherein said polyether is the product of the catalyzed alkoxylation of a monovalent alcohol having 8 to 30 carbon atoms with 20-200 moles of an alkylene oxide mixture of ethylene oxide and propylene oxide per mole of said monovalent alcohol, the molar ratio of ethylene oxide to propylene oxide in the alkylene oxide mixture being in the range of 30 : 70 to 90 : 10, the alkoxylation being carried out under pressure in the presence of from 0.2 to 0.5 weight percent of the catalyst relative to the alcohol used.
2. The thickener of claim 1, wherein the alkoxylation is carried out under a pressure of from 3 to 5 bar.
3. The thickener of claim 1, wherein said alcohol has 12 to 18 carbon atoms.
4. The thickener of claim 1, wherein 60 to 120 moles of said alkylene oxide mixture are used per mole of the alcohol.
5. The thickener of claim 1, wherein said molar ratio of ethylene oxide to propylene oxide is in the range of 50 : 50 to 90 : 10.
6. The thickener of claim 6, wherein said range is 70 : 30 to 85 : 15.
7. The thickener of claim 1, wherein said diisocyanate is hexamethylene diisocyanate.

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8. The thickener of claim 1, wherein said alcohol is tallow alcohol.
9. The thickener of claim 1, wherein said alcohol is lauryl alcohol.
10. A method of thickening an aqueous system, comprising adding a liquid thickener to the system, the liquid thickener comprising the diurethane reaction product of a polyether and a diisocyanate in a molar ratio of 1 : 0.7 to 1 : 0.25, wherein said polyether is the product of the catalyzed alkoxylation of a monovalent alcohol having 8 to 30 carbon atoms with 20-200 moles of an alkylene oxide mixture of ethylene oxide and propylene oxide per mole of said monovalent alcohol, the molar ratio of ethylene oxide to propylene oxide in the alkylene oxide mixture being in the range of 30 : 70 to 90 : 10, the alkoxylation being carried out under pressure in the presence of from 0.2 to 0.5 weight percent of the catalyst relative to the alcohol used.
11. The method of claim 10, wherein the liquid thickener comprises a mixture of liquid thickeners.
12. The method of claim 11, further comprising the step of adding a solubilizer to the aqueous system.
13. The method of claim 12, wherein the solubilizer comprises an alcohol alkoxylate.



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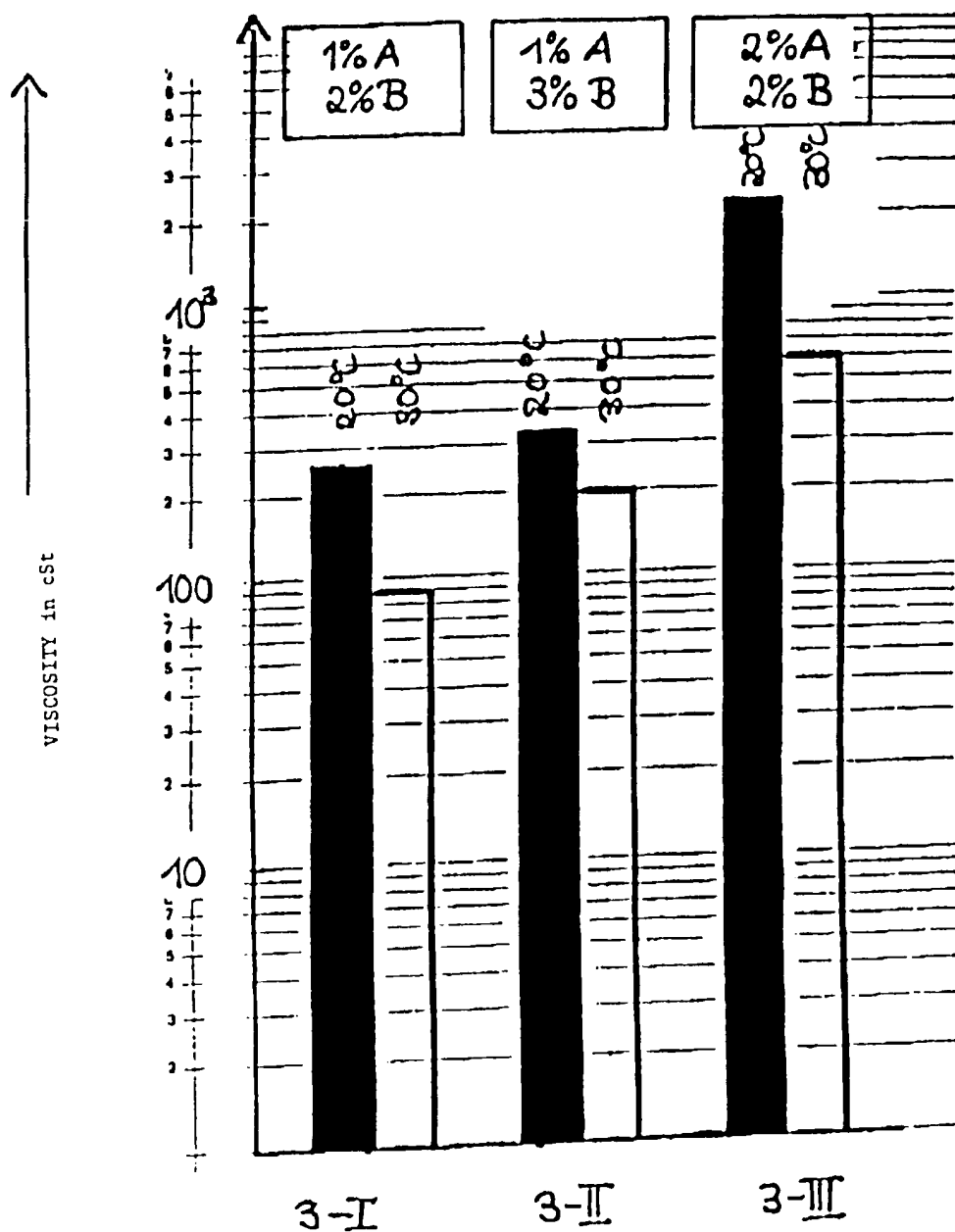


Figure 1: Viscosity of various citric acid solutions (5%) as a function of thickener concentration and temperature.

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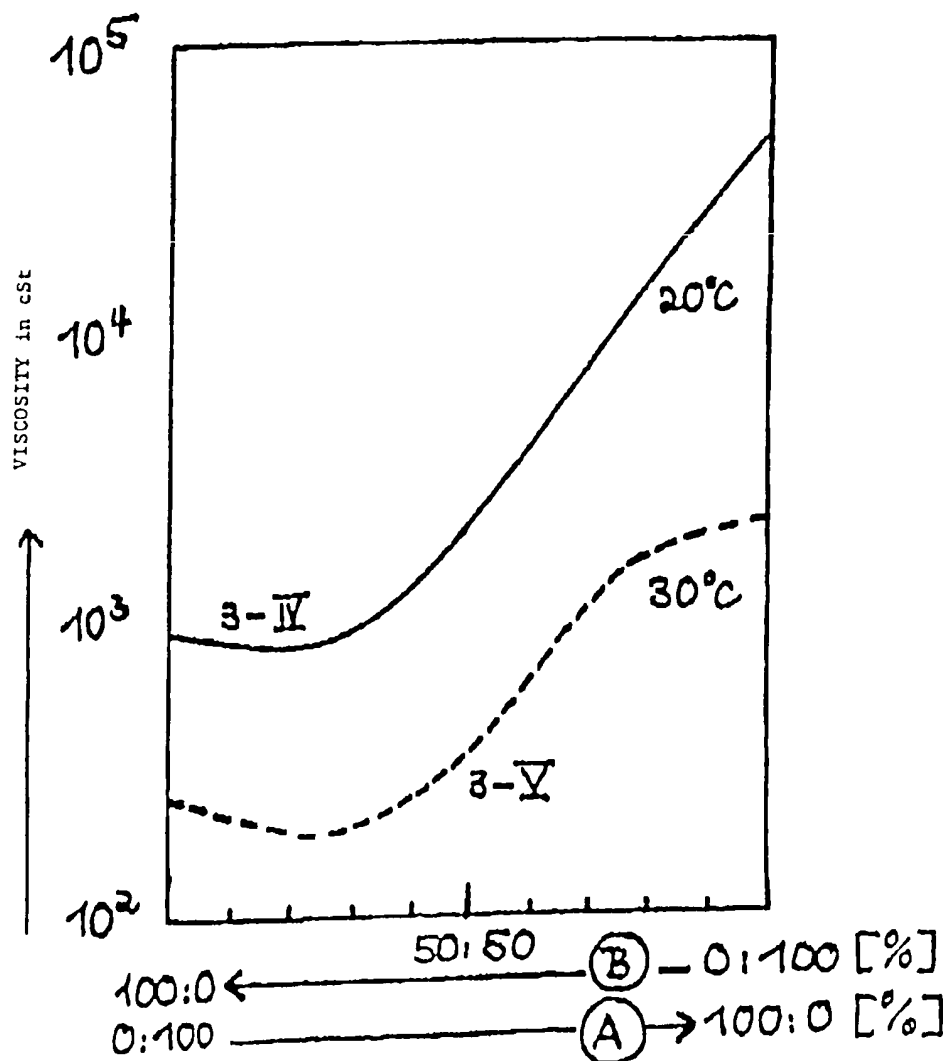


Figure 2: Viscosity of 14% ether sulfate solutions as a function of thickener concentration and temperature.

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